



## PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

## Method of Reactivating Oxidation Catalysts

We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organized under the Laws of the State of Delaware, United States of America, of No. 30 Algonquin Road, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

The present invention relates to the regeneration or reactivation of catalytic contact masses which have become contaminated with lead as a consequence of exposure to contact with lead-containing automotive exhaust gases incident to the catalytic oxidation of combustible components present in said exhaust gases.

It is now recognized that the elimination of certain components present in automotive exhaust gases is highly desirable and of prime importance in protecting the public health and welfare. The unavoidably incomplete combustion of hydrocarbon fuels by the gasoline or diesel engine results in the generation of substantial quantities of unburned hydrocarbons and other undesirable materials which, as waste products, are released to the atmosphere through the exhaust line. With the ever-increasing concentration of automobiles, particularly in urban areas, the discharge of such waste products into the atmosphere may reach significantly deleterious proportions. These combustion products are believed to react with atmospheric oxygen, under the influence of sunlight, to produce what is now commonly referred to as smog. Such combustion products include, by way of example, unsaturated hydrocarbons, partially oxidized hydrocarbons such as alcohols, ketones, aldehydes and acids, carbon monoxide, and various oxides of nitrogen and sulfur. Although at least a portion of these compounds may be partially removed by chemical sorption media, the conversion of exhaust gas constituents by catalytic means is the preferred technique. The

desired objective is to achieve substantially complete oxidation of all of the unburned hydrocarbons, particularly the high molecular weight unsaturated hydrocarbons, and carbon monoxide, as well as the partially-oxidized hydrocarbons hereinabove set forth, into carbon dioxide and water prior to discharging the exhaust gases into the atmosphere.

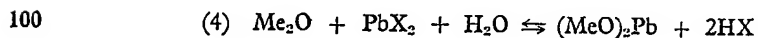
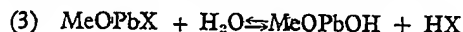
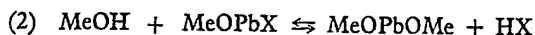
Catalytic means for improving waste products for discharge into the atmosphere, and particularly for the conversion of the hydrocarbonaceous combustion products contained within the exhaust gases emanating from an internal combustion engine, necessitate the use of a catalyst possessing high degree of activity, and particularly stability, or capability or performing its intended function for an extended period of time. A wide variety of factors affect the stability of active catalytic composites, which factors are generally peculiar to the environment in which the catalyst is employed. In the conversion of hydrocarbonaceous combustion products emanating from an internal combustion engine, the actual operation of the engine must be considered. For example, such an engine is commonly operated over a wide range of speed and load conditions and, therefore, the combustion efficiency thereof correspondingly varies; the space velocity and temperature of the exhaust gases, as well as the concentration of combustible material therein, likewise vary over wide limits. The catalyst should be capable of withstanding high temperatures of the order of 870°C. to as high as 1090°C. without rapid thermal deactivation, and preferably should possess maximum activity at substantially lower temperatures. The catalyst should have a relatively low threshold-activation temperature in order that the conversion reactions be self-initiating within a minimum time following startup from relatively cold conditions. In general, it is desirable that the catalyst be satisfactorily active at temperatures within the range of about 95°C. to about 1090°C.

The catalyst is usually disposed as a confined particle-form bed disposed in a suitable container or catalytic converter which is installed in the engine exhaust line. The catalytic converter may be of the through-flow, cross-flow, or radial-flow design and, in the case of vehicular applications, may supplant or be combined with the usual acoustic muffler. In the majority of systems, secondary or combustion air is injected upstream of the catalytic conversion zone, usually by means of an aspirator or by external compressor means.

Many potentially good, high-activity catalysts have been developed which perform well even under the aforesaid adverse conditions, including catalysts containing an active component selected from the metals of the high-hand column of Group I, the left-hand columns of Groups V and VI, and Group VIII of the Periodic Table of Elements. Such catalysts are nevertheless deleteriously affected by lead and lead compounds which are present as vapors or as entrained solids in the exhaust gases resulting from the combustion of a leaded fuel. The majority of motor fuels, including some fuels for marine engines, contain tetraethyl lead or equivalent lead compounds as an additive for increasing the antiknock efficiency of the engine in which the fuel is consumed. A typical commercial tetraethyl lead additive contains, in addition, approximately 2 gram-atoms of chlorine and 1 gram-atom of bromine, usually as ethylene dihalide, per gram-atom of lead, which is thus 1.5 times the stoichiometric quantity of halogen required to form the lead dihalide; in conventional terminology, the tetraethyl lead additive is said to contain 1.5 "theories" of halogen. The halogen serves as a scavenging agent to prevent buildup of lead deposits on spark plugs and engine cylinder walls by preferentially converting the lead tetraethyl, under the elevated cylinder temperatures prevailing during combustion, to highly volatile lead halides, for example, to lead chloride and lead bromide or to the oxyhalides of lead; minor quantities of lead do not react with halogen and are converted

instead to less volatile lead oxides. The major proportion of these lead compounds are discharged, as vapors or fines, into the exhaust line along with the exhaust gases. When the resulting lead-contaminated exhaust gases pass into contact with the exhaust gas conversion catalyst, the stability of the catalyst is substantially impaired, which phenomenon is demonstrated by the fact that the catalyst deactivation rate is very much greater than when unleaded fuel is employed.

On its face, this result would appear quite anomalous since most of the lead enters the conversion zone as a halide, and the normal catalyst bed temperature is in the range of 260°C. to 870°C., at which temperatures such halide volatiles. Therefore, one would expect the lead halide to pass completely through the bed with as much facility as it escaped deposition upon the engine cylinder walls and exhaust manifold structure. Such, however, is not the case. Although various theories have been proposed to explain the deactivation of catalysts by lead, it appears that the principal mechanism by which catalyst poisoning or deactivation occurs is one of chemical reaction between the volatile lead compounds and the catalyst base whereby to yield a stable, relatively non-volatile lead compound-catalyst base complex and/or form a monomolecular film of complex over the entire microstructure of the catalyst. Evidence favors the latter theory because, in most instances, physical measurements of spent lead-contaminated catalyst reveal no appreciable reduction in surface area or pore volume as compared to fresh catalyst. By catalyst base is meant a refractory inorganic oxide carrier or support, preferably of medium to high surface area, with which one or more catalytically active metals are composited. Typical bases include, for example, alumina, titania, silica, alumina-silica, alumina-zirconia and alumina-silica-zirconia. The deactivation of the catalyst is believed to proceed via the following reactions which are exemplary but not exhaustive of the several interactions of lead compounds with catalyst bases:



where Me represents an equivalent of a metallic component of the catalyst base, for example, Al, Zr or Ti, and X is a halogen, for example, chlorine, bromine or iodine.

Water, in the vapor or superheated vapor state, enters into reactions (3) and (4), supra,

which water is inevitably present in hydrocarbon combustion products. When the catalyst accumulates an average lead content within the range of 5% to 30%, by weight, and, more commonly, 10% to 25% by weight, which may occur after from 1600 to 32,000 road

kilometers of operation, depending upon the presence or absence of catalyst guard media, average space velocity, concentration of lead in the fuel, physical and/or chemical properties of the catalyst, and various other factors, the hydrocarbon and carbon monoxide conversion activities of the catalyst have usually fallen to such a low value as to preclude continued use, and such lead-contaminated catalyst must therefore be replaced with fresh catalyst or reactivated.

The instant invention provides a method for reactivating an oxidation catalyst containing at least one active component selected from metals of the right-hand column of Group I, the left-hand column of Groups V and VI, and Group VIII of the Periodic Table of Elements, said catalyst having been deactivated by exposure to lead-containing automotive exhaust gases, which comprises treating said catalyst with an aqueous solution of a compound of the group consisting of the polycarboxylic-acids and salts thereof and the hydroxymonocarboxylic acids containing not more than 4 hydroxyl groups and salts thereof, separating the treated catalyst from the solution, and drying the catalyst.

Experimental data have shown that when a catalyst is exposed to contact with a preponderance of plumbiferous gases, the lead content of the catalyst eventually stabilizes at an equilibrium level, usually in the range of from about 10% to about 25% by weight of lead, in a manner somewhat analogous to the deposition of coke upon cracking catalyst with the resultant attainment of "equilibrium" catalyst.

Prior art methods of regenerating a lead-contaminated catalyst are concerned with more or less complete removal of the lead by treating the catalyst with medium to strong acids such as nitric acid, hydrochloric acid or aqua regia. However, these reagents will also attack, by way of dissolution or oxidation or both, many of the components most beneficially employed in oxidation catalyst such as alumina, magnesia, titania, zirconia, copper, silver, gold, the iron group metals and oxides thereof, and to a lesser extent the platinum group metals. While the removal of lead may be substantially complete, there often results the concurrent loss of valuable catalytic constituents and/or an adverse chemical or physical change in the treated catalyst.

The relatively weak polycarboxylic and hydroxy-monocarboxylic acids utilized according to the instant invention, on the other hand, are extremely advantageous in that they cause no appreciable loss of catalytic constituents.

The precise effect of the polycarboxylate and hydroxymonocarboxylate solutions upon a lead compound-catalyst base complex is not known. It is established, however, that improved catalytic activity and any substantial

degree of lead removal are not necessarily concomitant. For this reason it is believed that the solutions may convert the several compound-catalyst base complexes to a form or forms of lead which exert a substantially lessened deactivating effect upon the catalyst. While in some instances it is possible to accomplish more or less complete removal of lead from the catalyst by practice of this invention, it should be emphasized that such lead removal is not necessary to the successful utilization thereof. The instant method is, of course, applicable both to reactivation in situ and to external reactivation.

The method of the present invention and the benefits afforded through the utilization thereof will be more clearly understood by defining several of the terms employed within the specification and the appended claims. The term "catalyst" or "oxidation catalyst" is intended to connote an element, compound, composite of two or more elements or compounds, or mechanical mixture of elements, compounds or composites containing a metal selected from the right hand column of Group I, the left hand column of Groups V and VI, and Group VIII of the Periodic Table of Elements, and which catalysts are employed for their catalytic activity in the oxidative conversion of various waste products, particularly hydrocarbons, oxyhydrocarbons, and/or carbon monoxide contained in automotive exhaust gases. The term "lead," "lead-containing" and "lead-contaminated" refer to metallic lead, lead compounds, particularly lead salts such as the sulfates and halides thereof, lead oxides, lead oxyhalides, mixtures of two or more such lead compounds and lead- or lead salt-catalyst complexes, since the actual form or forms in which the lead may exist in the exhaust gases or in combination with the catalyst are not definitely known.

Typical oxidation catalysts to which the present invention may be applied contain one or more catalytically active metallic components selected from the right hand column of Group I, the left hand column of Groups V and VI, and Group VIII of the Periodic Table of Elements, and which are preferably composited with a refractory inorganic oxide carrier material. Suitable catalytically active metallic components include, but are not limited to, vanadium, chromium, molybdenum, tungsten, members of the iron group and platinum group of the Periodic Table, copper, silver and gold. A particular metal may be used singly or in combination with any of the foregoing metals. Especially desirable catalytically active metals or combinations thereof comprise the following: platinum, palladium, other noble metals such as iridium and rhodium, iron, cobalt, nickel, chromium, copper, vanadium, tungsten, molybdenum, manganese,

silver, gold and various mixtures including copper-cobalt, copper-iron, copper-chromium, nickel-chromium, cobalt-chromium, manganese-chromium, manganese-iron, platinum-iron, platinum-cobalt, platinum-nickel, palladium-iron, palladium-cobalt, palladium-nickel, palladium-copper, palladium-platinum, palladium-copper-cobalt, platinum-copper-cobalt, copper-cobalt-nickel-palladium and platinum-palladium-cobalt. A most advantageous catalyst consists essentially of a composite of an alumina carrier and from 0.01 to 10% by weight of a noble metal.

As hereinabove set forth, the catalytically active metallic component or components are desirably composited with a refractory inorganic oxide, the latter serving as a carrier material therefor. Although greater stability and activity are usually obtained when the refractory inorganic oxide contains at least a portion of alumina, other suitable refractory inorganic oxides may be employed including silica, boria, titania, zirconia, hafnia, and mixtures of two or more. These materials may be of synthetic origin or they may be naturally occurring substances such as clays or earths, and may or may not have been activated prior to use.

The catalytically active metallic components may be composited with the carrier material by any of the known methods involving precipitation and/or impregnating techniques. Platinum, for example, may be added to the carrier material by commingling the latter with an aqueous solution of chloroplatinic acid. Other water-soluble compounds of platinum, or of other noble metal components, may be utilized within the impregnating solution. When the catalyst is to contain other metallic components, the catalyst may be prepared by commingling soluble compounds of these components, particularly the nitrates, chlorides or carbonates, and soaking the particles of the inorganic refractory oxide therein, followed by heating to form the corresponding oxides of the metallic components. Alternatively, one or more impregnating solutions containing one or more of the catalytically active metallic components may be used successively.

The polycarboxylic acids which may be used in aqueous solution, to treat the deactivated catalyst, that is, catalyst which has been exposed to contact with lead-containing exhaust gases under conversion conditions for sufficient time as to become substantially deactivated, include aryl, alicyclic and aliphatic polycarboxylic acids, hydroxypolycarboxylic acids, water-soluble salts and acid salts of polycarboxylic and hydroxy polycarboxylic acids including the sodium, potassium, lithium and ammonium salts thereof, and water-soluble salts of aminopolycarboxylic acids.

Of the aryl carboxylic acids, representative

compounds are phthalic acid, isophthalic acid and terephthalic acid. In general, it is preferable to employ the alkali metal or ammonium salts of the aryl polycarboxylic acids, since the acids themselves have only a very limited solubility in water.

Of the alicyclic polycarboxylic acids, representative compounds are 1,1-cyclopropanedicarboxylic acid, 1,2,3-cyclopropanetricarboxylic acid, 1,2-cyclobutanedicarboxylic acid, 1,3-cyclobutanedicarboxylic acid, 1,2-cyclopentanedicarboxylic acid, 1,3-cyclopentanedicarboxylic acid and 1,4-cyclohexanedicarboxylic acid. Many of the foregoing polycyclic polycarboxylic acids has cis and trans stereoisomers, and the use of these also is included within the scope of the invention.

Of the aliphatic polycarboxylic acids, representative compounds are oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, and pimelic acid.

Of the hydroxypolycarboxylic acids, exemplary compounds are malic acid, citric acid and tartaric acid, including the optical isomers thereof.

The water-soluble salts of aminopolycarboxylic acids, and more particularly, the water-soluble salts of the aliphatic and aryl-diaminopolycarboxylic acids may likewise be utilized in the aqueous regenerating medium, although not necessarily with identical results. Exemplary acids of this class are ethylenediaminetetracarboxylic acid, ethylenediaminetetraacetic acid, ethylene-diamine-tetrapropionic acid, ethylenediaminetetrabutyrac acid, propylenediaminetetracarboxylic acid, propylenediaminetetraacetic acid, propylenediaminetetrapropionic acid, butylenediaminetetracarboxylic acid, butylenediaminetetraacetic acid, butylenediaminetetrapropionic acid and phenylenediamine tetracarboxylic acid.

Where a water-soluble salt is employed, such salt may be neutral or acid, that is, all or less than all of the replaceable hydrogen atoms of the polybasic acid may be replaced with a suitable cation; for example, potassium oxalate or potassium acid oxalate may be utilized.

The other type of compound which is used in aqueous solution, to treat the deactivated catalyst in accordance with the invention, comprises a hydroxymonocarboxylic acid, preferably an  $\alpha$ -hydroxymonocarboxylic acid, containing not more than 4 hydroxyl groups, or a water-soluble salt of such acid, such as the sodium, potassium, lithium and ammonium salts thereof. Exemplary but not necessarily equivalent compounds include glycollic acid, lactic acid, beta-hydroxypropionic acid, alpha, beta-dihydroxypropionic acid, alpha-hydroxybutyric acid, beta-hydroxybutyric acid, gamma-hydroxybutyric acid, alpha, beta-dihydroxybutyric acid, alpha, gamma-dihydroxybutyric

acid, beta, gamma-dihydroxybutyric acid, trihydroxybutyric acid, alpha-hydroxyisobutyric acid, and beta-hydroxyisobutyric acid. In addition to such aliphatic hydroxycarboxylic acids, aryl-aliphatic hydroxymonocarboxylic acids such as phenylglycollic acid, tolylglycollic acid, and xylglycollic acid may also be employed. Many of these compounds have stereoisomers and these are also included within the scope of the invention; for example, the dextro-, laevo-, and inactive forms of lactic acid all give good, though not equal, results.

Hydroxymonocarboxylates containing more than 4 hydroxyl groups, such as gluconic acid (pentahydroxy-n-caproic acid), have been found to be inoperable for reasons unknown, and the class of compounds of this invention is therefore limited to those having less than 5 hydroxyl groups.

The aqueous solution employed for regeneration may contain, in varying proportions, two or more different acids, or a mixture of one or more acids and salts, or two or more salts. The concentration of acid or salt is not particularly critical and may range from quite dilute up to the limit of saturation at the solution temperature. Very good results have been achieved with solutions containing from about 0.5% to about 10% by weight of acid or salt. The temperature of the solution may range from room up to about 95°C. or more, provided that the temperature is not so high as to cause dehydration or decomposition of the hydroxy acid; solution temperatures of from 38°C. to 95°C. are preferred because the regenerating reactions proceed more rapidly than at lower temperatures and the time required for contacting the catalyst is correspondingly reduced. When a particular catalyst is quite susceptible to acid attack, the acid solution may be buffered by commingling therewith ammonium hydroxide or an alkali metal hydroxide. The spent catalyst may be contacted with the solution for a period of from 10 minutes to 3 hours or more; the solid-liquid contacting may be accomplished batchwise in a suitable treating vessel, or continuously in a co-current or counter-current contacting tower or moving belt-type apparatus, or in situ by providing the converter with suitable flushing connections for passing the regenerating solution therethrough. Following the treatment with the solution acid, particularly where the solution contains alkali metal ions, it is usually desirable to remove these metal ions by washing, preferably with water, and filtering the freshly treated catalyst one or more times. If no metal ions are present, washing is usually unnecessary and the excess organic material may be driven off by drying or calcining the freshly treated catalyst at a suitably high temperature, for example, at a temperature of from about 315°C. to about 427°C. or higher, the calcining being preferably effected at a temperature above 427°C.

Such drying may be accomplished by ordinary heating means such as a muffle furnace or the wet catalyst may be dried in situ by passage of hot exhaust gases through the converter bed to the normal operation of the catalytic converter.

The following examples are given for the purpose of further illustrating the method of the present invention.

#### EXAMPLE I

A spherical catalyst comprising 0.2% Pt and 10% CoO deposited on a refractory oxide base consisting of 2% silica and 98% alumina was contaminated with lead by prolonged exposure to lead - containing exhaust gases emanating from an internal combustion engine using leaded fuel. A portion of the leaded catalyst was divided into seven samples, each 65 cc. in volume and weighing about 20 grams, being designated as catalyst samples A through G in Table I below. Catalyst sample A was contacted for about 2 hours at a temperature of 77°—93°C. with a solution containing 4 grams of tartaric acid dissolved in 200 cc. of water. Following this treatment the tartaric acid solution was decanted and the treated catalyst washed four times with 100 cc. volumes of water. The washed catalyst was then dried and ignited in a muffle furnace for 1 hour at 538°C.

Catalyst sample B was similarly treated except that citric acid was used in place of tartaric acid.

Catalyst sample C was similarly treated with an aqueous solution of citric acid plus sufficient ammonium hydroxide to neutralize the two hydrogen ions of the citric acid molecule.

Catalyst sample D was similarly treated with an aqueous solution of citric acid plus an equimolar quantity of ammonium sulfate.

Catalyst sample E was similarly treated, except that the regenerating solution contained oxalic acid.

Catalyst sample F was treated with an aqueous solution of ethylenediaminetetraacetic acid (EDTA) with sufficient ammonium hydroxide added thereto to solubilize the EDTA.

Catalyst sample G was treated with an aqueous solution containing the tetrasodium salt of ethylenediaminetetraacetic acid.

The activity of the untreated and treated catalysts, as well as that of fresh catalyst, was tested by measuring the ignition temperature and temperature rise obtained by passage of air containing benzene vapor, under standardized conditions, into and through an apparatus in which a bed of the catalyst was gradually heated until ignition of the benzene vapor occurred (as indicated by development of a temperature differential between the bed inlet and bed outlet). A small temperature rise and/or a high ignition temperature indicate

a low conversion activity. A correlative evaluation of catalytic mufflers operated on both test automobiles and on dynameter stands has shown that a catalyst, when subjected to the foregoing benzene oxidation test, must have an ignition temperature of less than about 316°C. and a temperature rise above about 195°C. to perform satisfactorily as an exhaust gas oxidation catalyst.

A comparison of the activities of fresh catalyst, spent catalyst and regenerated catalyst are shown in Table I.

TABLE I

	Fresh	A	B	C	D	E	F	G
Catalyst Sample before Reactivation								
Lead, weight—%	0	17.5						
Ignition Temp., °C.	204	above 538						
Temp. Rise., °C.	334	0	0	0	0	0	0	0
After Reactivation								
Lead, weight—%	—	8.4	10.8	5.8	15.7	16.1	3.7	8.6
Ignition Temp., °C.	—	288	174	196	174	180	174	193
Temp. Rise, °C.	—	230	225	256	278	233	242	250

It will be observed that all of the catalyst samples showed a substantial improvement in catalytic activity, notwithstanding the fact that the degree of lead removal was far from complete in each instance. In particular, samples D and E, which were treated with rather strongly acidic solutions in comparison with the other samples, underwent very little lead removal yet showed a surprisingly high activity following reactivation. In all cases excepting the treatment with tartaric acid, the ignition temperature of the regenerated catalyst was substantially lower than that of the fresh catalyst.

## EXAMPLE II

In order to determine whether a catalyst

could be regenerated without removing any lead at all therefrom, the following experiment was devised; a sample of the spent catalyst of Example I was placed in a rotating autoclave together with an aqueous solution of oxalic acid containing 2% by weight of oxalic acid. The solid-liquid mixture was evaporated to dryness so that there was no possibility of lead removal, the leaded catalyst being simply impregnated with oxalic acid. The dried catalyst was then calcined for 1 hour at 538°C.

The treated catalyst was then subjected to the benzene oxidation test set forth in Example I, supra; the activities of fresh catalyst, spent leaded catalyst, and impregnated leaded catalysts are compared in Table II:

TABLE II

Catalyst Sample	Activity Before Impregnation		Impregnating Reagent	Activity After Impregnation	
	Ignition Temp. °C.	Temp. Rise °C.		Ignition Temp. °C.	Temp. Rise °C.
Fresh	204	334	—	—	—
Spent	above 538	0	Oxalic Acid	221	228

It is clear that the present invention is completely operable even without removing lead and that, upon completion of the solid-liquid contacting step, it is immaterial whether

the regenerating solution be separated from the catalyst by filtration or by evaporation.

### EXAMPLE III

It was desired to ascertain the activity and stability of regenerated catalyst under typical exhaust gas conversion conditions. This was accomplished by means of a standard test designed to simulate conditions which would be encountered in the course of the actual operation of a motor vehicle. The exhaust gases from a spark-ignition engine running on leaded gasoline and loaded by a dynamometer-generator were passed through three parallel-connected converters; a constant flow of secondary air was passed into the inlet of each converter.

Converter No. 1 contained a bed of fresh spherical catalyst comprising 0.2% Pt and 10% CoO on a silica (2%)-alumina (98%) base. Converter No. 2 contained catalyst of the same initial composition but which had been deactivated by prolonged exposure to plumbiferous exhaust gases during a preceding run. Converter No. 3 contained leaded catalyst from the same batch as that of converter No. 2, but which had been reactivated with a citric acid solution according to the technique described in Example I, supra. The volumes of the three catalyst beds were equal, and the exhaust flow rates were carefully controlled to insure uniformity of space velocity.

The engine was run at 2500 rpm and 41 brake horse power for a period of 60 hours.

At 0 hours, 40 hours and 60 hours, samples of the inlet and outlet gases entering and leaving each converter were periodically withdrawn and analyzed for hydrocarbon content by a non-dispersive infra-red gas analyzer employing a hexane cell detector. By the difference between hydrocarbon content of inlet and outlet samples, the percent hydrocarbon conversion was thus determined at the stated intervals during the test run, and the decline in catalyst activity as a function of time readily observed therefrom. In reporting the results of the analyses performed on the exhaust gas samples, the term "hydrocarbon" connotes all hydrocarbons whether saturated, unsaturated, or partially oxidized, as determined by the aforementioned analytical method.

A comparison of the percent hydrocarbon conversions for the fresh, spent and regenerated catalyst samples is shown in Table III below: the stabilities of the fresh and regenerated catalyst samples are also compared. The stability is calculated from a semi-logarithmic plot of percentage conversion on the ordinate against time on the abscissa, which yields an approximately straight line of negative slope since the manner of catalyst deactivation is essentially a first-order mechanism. The stability is then taken as the reciprocal of the absolute value of the slope, a gradual slope showing a high stability and a steep slope a low stability.

TABLE III

Converter	Catalyst	Percent Hydrocarbon Conversion			
		0 Hrs.	40 Hrs.	60 Hrs.	Stability
#1	Fresh	74.8	55.0	32.5	31.3
#2	Spent	20.3	22.5	26.8	—
#3	Regenerated	69.1	52.4	32.5	50.3

It will be noted from the data in the above table that the initial activity of the regenerated catalyst is very nearly that of the fresh catalyst. Furthermore, the stability of the regenerated catalyst is about 16% greater than that of the fresh catalyst which is probably due to the fact that the regenerated catalyst already contained considerable lead and therefore initially approached more closely the equilibrium lead level.

### EXAMPLE IV

Another portion of the substantially deactivated, leaded catalyst of Example I was divided into three samples, each 65 cc. in

volume and weighing about 20 grams, designated catalyst J, catalyst K, and catalyst L in Table IV below. Catalyst J was contacted for about 2 hours at a temperature of 77-93°C. with a solution containing 4 grams of lactic acid dissolved in 200 cc. of water. Following this treatment the lactic acid solution was decanted and the treated catalyst washed 4 times with 100 cc. volumes of water. The washed catalyst was then dried and ignited in a muffle furnace for 1 hour at 538°C.

Catalyst K was similarly treated except that gluconic acid,  $\text{CH}_2\text{OH}(\text{CHOH})_4\text{COOH}$ , was used in place of lactic acid.

Catalyst L was similarly treated except

that sodium glucoheptonate  $\text{CH}_2\text{OH}(\text{CHOH})_5\text{COONa}$ , the principal constituent of a well known sequestering agent, was employed instead of lactic acid.

- 5 The activity of the untreated and treated catalysts, as well as that of the fresh (un-

lead) catalyst, was tested in the same manner as described in Example I.

The conditions of treatment of the deactivated catalyst and a comparison of the activities of fresh catalyst and regenerated catalyst are shown in Table IV. 10

TABLE IV

	Fresh	J	K	L
Catalyst Sample Before Reactivation				
Lead, weight—%	0	17.5	17.5	17.5
Ignition Temp., °C.	204	above 538		
Temp. Rise, °C.	334	0	0	0
Reactivating Treatment				
Grams Reagent per 100 cc. $\text{H}_2\text{O}$	—	2	2	2
Contacting Time, hours	—	2	2	2
After Reactivation				
Lead, weight—%	—	5.8	12.8	16.8
Ignition Temp., °C.	—	190	354	above 482
Temp. Rise, °C.	—	361	39	0

- 15 It may be seen the catalyst J, which was treated with a lactic acid solution, had a higher activity than the fresh catalyst even though it still contained a substantial quantity of lead after treatment. On the other hand, catalyst K, which was treated with gluconic acid solution, and catalyst L, which was treated with sodium glucoheptonate solution, showed very little improved activity, demonstrating that a hydroxymonocarboxylic containing more than 4 hydroxyl groups is virtually inoperable for the instant purpose of regenerating a lead-contaminated catalyst. 20 25

#### EXAMPLE V

- 30 A lead-contaminated catalyst having an original (unleaded) composition of 1% Pt plus 1% Pd on a silica-alumina-zirconia base was treated for 1 hour with an aqueous ammonium lactate solution containing 3% ammonium lactate by weight and maintained at about 66°C. The dried catalyst, when employed in a catalytic muffler, shows a substantial improvement in exhaust gas oxidation activity. 35

#### EXAMPLE VI

A spent lead-contaminated catalyst having

an original composition of 0.5% Pt and 20% CuO on a silica-alumina base was contacted for 2 hours with a heated aqueous 1% solution of sodium dihydroxypropionate. The treated catalyst was removed from the solution, washed with water, filtered, and dried for 2 hours at 482°C. The resulting regenerated catalyst, when contacted with a mixture of air and exhaust gases at an elevated temperature, shows a substantially improved exhaust gas oxidation activity. 40 45

#### EXAMPLE VII

50 A catalytic composite comprising 0.1% Pt and 10%  $\text{V}_2\text{O}_5$  impregnated on an alumina-zirconia base and having the form of 3.2 mm spheres was employed for the catalytic oxidation of plumbiferous exhaust gases emanating from an internal combustion engine using leaded fuel. The average power output of the engine is 41 brake horsepower at 2500 rpm, and after 60 hours' operating time the catalyst was nearly completely deactivated. The catalyst was treated for 2 hours at 66°C. in a treating tank containing a 2% solution of glycollic acid in water, buffered with  $\text{NH}_4\text{OH}$  to a pH of 7.5. The dried, regenerated cata- 55 60



lyst shows increased hydrocarbon and carbon monoxide conversion activity.

# WHAT WE CLAIM IS:—

1. A method of reactivating an oxidation catalyst containing at least one active component selected from metals of the right-hand column of Group I, the left-hand column of Groups V and VI, and Group VIII of the Periodic Table of Elements, said catalyst having been deactivated by exposure to lead-containing automotive exhaust gases with resultant deposition of lead on said catalyst, which comprises treating said catalyst with an aqueous solution of a compound of the group consisting of the polycarboxylic acids and salts thereof and the hydroxymonocarboxylic acids containing not more than 4 hydroxyl groups and salts thereof, separating the treated catalyst from the solution, and drying the catalyst.
2. The method of claim 1, wherein the catalytically active metallic component is composited with a refractory oxide carrier, and the reactivation is effected by treating the deactivated catalyst with an aqueous solution of substantially from 0.5 to 10% by weight of the acid or salt at a temperature of from room temperature to 95°C., and for a time period of from 10 minutes to 3 hours.
3. The method of claim 2, wherein the catalyst consists essentially of a composite of an alumina carrier and from 0.01 to 10 weight percent of a noble metal.
4. The method of any of the claims 1 to 3, wherein the active metallic component is platinum.
5. The method of any of the claims 1 to 4 further characterized in that the deactivated catalyst is treated with an aqueous solution of an aliphatic polycarboxylic acid.
6. The method of Claim 5 further characterized in that the deactivated catalyst is treated with an aqueous solution of oxalic acid.
7. The method of any of the claims 1 to 4 further characterized in that the deactivated catalyst is treated with an aqueous solution of a hydroxypolycarboxylic acid.
8. The method of claim 7 further characterized in that the deactivated catalyst is treated with an aqueous solution of tartaric acid.
9. The method of claim 7 further characterized in that the deactivated catalyst is treated with an aqueous solution of citric acid.
10. The method of any of the claims 1 to 4 further characterized in that the deactivated catalyst is treated with an aqueous solution of a salt of an aliphatic polycarboxylic acid.
11. The method of claim 10 further characterized in that the deactivated catalyst is treated with an aqueous solution of ammonium citrate.
12. The method of any of the claims 1 to 4 further characterized in that the deactivated catalyst is treated with an aqueous solution of a salt of an aliphatic aminopolycarboxylic acid.
13. The method of claim 12 further characterized in that the deactivated catalyst is treated with an aqueous solution of an ammonium or alkali metal salt of an aliphatic diaminotetraacetic acid.
14. The method of any of the claims 1 to 4, further characterized in that the deactivated catalyst is treated with an aqueous solution of an  $\alpha$ -hydroxymonocarboxylic acid.
15. The method of claim 14, further characterized in that the deactivated catalyst is treated with an aqueous solution of glycollic acid.
16. The method of claim 14, further characterized in that the deactivated catalyst is treated with an aqueous solution of lactic acid.
17. The method of claims 1 to 4, further characterized in that the deactivated catalyst is treated with an aqueous solution of ammonium lactate.
18. The method of claims 1 to 17, further characterized in that following the separation of the catalyst from the aqueous solution, the catalyst is water-washed and calcined at a temperature above about 427°C.
19. The method of increasing the activity of an oxidation catalyst which has been deactivated by exposure to lead-containing automotive exhaust gases, substantially as claimed in claim 1 and as described.

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